DATA EVALUATION RECORD

STUDY 16

CHEM 036101 Trifluralin §165-1

FORMULATION--12--EMULSIFIABLE CONCENTRATE

STUDY ID 41661102
Rainey, D.P. 1990. Confined rotational crop study with ^{14}C trifluralin. Laboratory Project Identification ABC0411. Unpublished study performed by DowElanco and Eli Lilly and Company, Greenfield, IN, and submitted by the Trifluralin Data Development Consortium, Greenfield, IN.

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CONCLUSIONS:

Rotational Crops - Confined Accumulation

This accumulation in confined rotational crops study is scientifically valid and can be used as supplemental data. However, it cannot be used to fulfill data requirements (165-1) for the following reasons:

a. To relate the accumulation of [^{14}C]trifluralin and its degradates to applied test material in the soil, the soil analytical data are needed.

b. Since plant tissue samples were stored frozen for up to one year, data demonstrating that [^{14}C]trifluralin and its degradates are stable in plant tissue when stored frozen are needed.

c. In order to validate the analytical data, the separatory TLC data should be confirmed by another analytical methodology (preferably MS).

Trifluralin residues accumulated in Swiss chard (0.079 ppm), turnip roots (0.051 ppm), turnip leave (0.086 ppm), corn grain (0.007 ppm), and corn fodder (0.027 ppm) planted in treated soil 30 days posttreatment. In crops (Swiss chard, turnips, corn, and winter wheat) planted in treated soil at 108 to 361 days posttreatment trifluralin residues were ≤0.037 ppm. Char-

acterization of [^{14}C]residues indicated that extractable tissue residues were multicomponent in nature. However, non-extractable residues in 3-4 samples were associated with the legnin (7.6-25.6% of total ^{14}C-residue) fraction.

In rotational crops planted in treated soil 361 days posttreatment, total [^{14}C]residues had declined to 0.017 ppm in mature Swiss chard leaves, 0.008 ppm in turnip roots and leaves, 0.020 ppm in corn grain, and ≤0.009 ppm in corn silage and forage. ^{14}C-residues were not detected in corn grain planted at 361 days posttreatment.

Soil treated with trifluralin at 0.77 or 0.74 lb a.i./A was reported to contain in the surface soil (0 to 9 or 0 to 12 inches) immediately post-treatment [^{14}C]-trifluralin residues at levels of 0.738 lb a.i./A for the field soil used for the 213-day rotation; 0.773 lb a.i./A in the field soil used for the 30-day, 214-day, and 362-day rotations; and 0.818-0.863 lb a.i./A in the greenhouse soil used for the 30-day rotation. At 30-day posttreatment the greenhouse soil had reported [^{14}C]trifluralin at 0.56-0.60 lb/A and 0.28-0.346 lb/A at approximately 110 days. In the field soil, [^{14}C]trifluralin was 0.284 lb/A at 30 days and 0.116 lb/A at approximately 180 days. In the 108-, 174-, and 361-day rotation field soils, [^{14}C]trifluralin at planting and harvest (120-441 days posttreatment) was reported to ranged from 0.03 to 0.08 lb/A with no discernable pattern. In field soil, [^{14}C]trifluralin was reported at 0.223 lb/A at 213 days and 0.18-0.20 lb/A at ≈220-380 days.

METHODOLOGY:

Field experiment: Uniformly ring-labeled [^{14}C]trifluralin plus unlabeled trifluralin (purities 99.0 and 96.4%, respectively; final specific activity 1.89 uCi/mg, formulated as a 4 lb/gal EC) was applied at approximately 0.77 lb ai/A to a field plot (7 x 14 feet) of sandy loam soil (62% sand, 23% silt, 15% clay, 2.8% organic matter, pH 7.5, CEC 15.1 meq/100 g) using a compressed air sprayer. The plot, located in Marion, Indiana, was treated on May 6, 1988. Immediately after treatment, the soil was raked (mixing the upper 2-3 inches) and 10 soil cores (0- to 6-inch depth, 2-inch diameter) were collected. The treated area was then divided into subplots (each 4 x 6 feet; Plots 1, 2, and 4), which were enclosed with a wood border. An additional plot (Plot 3) adjacent to the original plots was treated with trifluralin at 0.74 lb ai/A on September 30, 1988. The pesticide was raked into the soil, and the soil was sampled as previously described.

At 30 days (Plot 1), 213 days (Plot 3, fall-applied), and 361 days (Plot 4) posttreatment, the treated soil was planted with Swiss chard, turnips, and corn. At 108 days posttreatment, Plot 2 was planted to Swiss chard and turnips; at 174 days, the same plot was planted to winter wheat. The Swiss chard and turnips in the 30-day rotation failed because of high summer temperatures and the experiment had to be repeated in the greenhouse (described below). Swiss chard and turnips were harvested when the plants were mature (65-73 and 80-88 days postplanting, respectively); corn was harvested when immature and at maturity (141-161 days postplanting); and wheat was harvested when immature and at maturity (244 days postplanting). Swiss chard (leaves), wheat (forage, or grain and straw), and corn (forage, silage, or grain and fodder) were collected by cutting the plants at a height of 2-3 inches above the soil surface and separating the various tissues. The turnip plants were removed whole from the soil and separated into roots and leaves. Soil cores (10/plot; 9-12 inches deep) were collected at time of treatment and at planting and harvest of each crop. Within 1 hour of collection,

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each soil core was placed in a jar and mixed with acetonitrile; the jars were then sealed and shaken.

Greenhouse experiment (30-day rotation): Sandy loam soil from untreated field plots was transferred into four pots (9-inch soil depth, 11.75-inch diameter) in the greenhouse, covered with a 3-inch layer of additional soil that had been treated at approximately 0.84 lb ai/A with ring-labeled [^{14}C]trifluralin on May 17, 1989, and aged for 30 days. Water was applied to the pots of soil immediately posttreatment, three times weekly during the aging period, and as needed (every 1-2 days) during plant growth. Swiss chard leaves and turnip roots and leaves were harvested when the plants were mature (54 and 75 days postplanting, respectively) as previously described. Three soil cores (0- to 6-inch depth) were collected from each pot at 2 hours posttreatment, at planting, and at harvest. Cores from each pot were pooled in a glass jar and mixed with acetonitrile; the jars were sealed, shaken on a rotary shaker for 30 minutes, and allowed to stand overnight.

Laboratory storage and analysis: The Swiss chard leaves, turnip leaves and roots, and wheat forage were rinsed, and, with the corn silage and forage, were frozen in liquid nitrogen, ground, and refrozen. The grain samples, wheat straw, and corn fodder were ground without prior freezing in liquid nitrogen, then frozen. Crop samples were stored frozen for up to 11 days prior to combustion analysis for total radioactivity, and for up to 1 year prior to residue characterization.

All plant samples were analyzed for total radioactivity using LSC following combustion. [^{14}C]Residue characterization was attempted using the four crop samples containing the highest concentration of [^{14}C]residues (Swiss chard leaves, turnip leaves, and turnip roots from 30-day planting; and wheat straw from 174-day planting). The Swiss chard and turnip tissues were extracted with methanol by stirring for 2 hours, then with methanol by refluxing for 1 hour. The wheat tissue was extracted with methanol:water (1:1) by stirring for 2 hours, then with methanol by refluxing for 1 hour. The extracts from each crop were filtered, combined, and concentrated. The concentrated extracts were diluted with water (1:1, v:v) and partitioned twice with an equal volume of methylene chloride. Aliquots of the methylene chloride fraction were concentrated and analyzed by LSC. The aqueous fraction was concentrated to remove the methanol, then partitioned twice with an equal volume of ethyl acetate. Aliquots of the ethyl acetate fraction were concentrated and analyzed by LSC. The remaining aqueous solution was acidified (pH 2) and again partitioned twice with an equal volume of ethyl acetate; the ethyl acetate fraction was concentrated and aliquots were analyzed by LSC. The extracted solution was neutralized and aliquots were analyzed by LSC. The concentrated plant extracts were dried onto silica gel, which was then placed at the top of columns previously packed with the same silica gel. The columns were sequentially eluted with hexane, hexane:toluene, toluene, toluene: ethyl acetate, ethyl acetate, ethyl acetate:methanol:water, methanol: water and methanol:glacial acetic acid. All fractions were collected, and aliquots were analyzed for total radioactivity by LSC. Fractions containing [^{14}C]residues were concentrated under vacuum and analyzed for trifluralin using one-dimensional TLC on silica gel plates developed in hexane:methanol (97:3, v:v). Radioactive zones on the plates were located using autoradiography, and trifluralin was identified by comparison to a reference standard that had been co-chromatographed with the sample. The zone containing trifluralin was scraped from the plate and quantified by LSC; the remaining portion

of the sample lanes were divided into zones, which were individually scraped from the plate and quantified by LSC.

The methanol-extracted plant tissue was divided into three portions. One portion was analyzed for total radioactivity using LSC. A second portion was refluxed overnight with 1.0 N hydrochloric acid. The acid extract was partitioned twice with ethyl acetate, and the extract and extracted solutions were analyzed by LSC. The acid-extracted plant tissue was analyzed for total radioactivity by LSC following combustion. In order to quantify the residues associated with lignin tissue, the third portion of the methanol-extracted plant tissue was mixed with prechilled 72% sulfuric acid and held at 5-7 C for approximately 24 hours. The mixture was then mixed with water and boiled for 2 hours. The insoluble lignin was collected on fritted glass filters, dried, weighed, and analyzed for total radioactivity by LSC following combustion.

Soil samples were filtered to separate the soil and the acetonitrile that had been added when the samples were collected. Aliquots of the acetonitrile were analyzed for total radioactivity by LSC; the extracted soil was air-dried and analyzed for unextracted [^{14}C]residues by LSC following combustion. Aliquots of the extracts from soil samples collected from the field plots at the time of planting and harvest were analyzed for trifluralin by one-dimensional TLC as previously described.

DATA SUMMARY:

[^{14}C]Trifluralin residues accumulated (up to 0.086 ppm) in Swiss chard and turnips that were planted in greenhouse pots of sandy loam soil, and in corn that was planted in a field plot of sandy loam soil 30 days following treatment of the soils with ring-labeled [^{14}C]trifluralin (radiochemical purity 99.0%, formulated as a 4 lb/gal EC) at a nominal rate of 0.825 lb ai/A. In crops (Swiss chard, turnips, corn, and winter wheat) planted 108 to 361 days after field plots of sandy loam soil were treated with [^{14}C]trifluralin at 0.825 lb ai/A, [^{14}C]trifluralin residues were $\leq$0.037 ppm. Analysis of organic extracts from the four plant tissues containing the highest concentrations of [^{14}C]residues detected no compound present at >0.012 ppm. Lignin comprised 7.6-25.6% of the total [^{14}C]residues in the plants (Table 14).

In the 30-day rotation, total [^{14}C]residues were 0.073 ppm in mature Swiss chard leaves, 0.051 ppm in turnip roots, 0.086 ppm in turnip leaves, 0.007 ppm in corn grain, and 0.027 ppm in corn fodder (Table 3). Total [^{14}C]residues were 0.015-0.016 ppm in immature corn forage and silage. In the Swiss chard and turnips, 42.9-57.7% of the recovered [^{14}C]residues were methanol-extractable (0.020-0.027 ppm organosoluble, 0.004-0.016 ppm aqueous soluble; Table 8). Chromatography of the organosoluble fraction indicated that no [^{14}C]residues were >0.018 ppm; the aqueous soluble [^{14}C]residues were not further analyzed (Tables 9-11).

In the 108-day rotation, [^{14}C]residues were not detected in mature Swiss chard leaves and turnip roots and leaves (Table 5).

In the 174-day rotation interval, total [^{14}C]residues were 0.037 ppm in mature wheat straw and were not detected in wheat grain (Table 5). Total [^{14}C]residues were 0.010 ppm in the immature wheat forage. In the wheat straw, 48.4% of the recovered [^{14}C]residues were methanol-extractable (0.011 ppm organosoluble, 0.006 ppm aqueous soluble; Table 8). Chromatography of the organosoluble fraction indicated

that no [^{14}C]residues were >0.004 ppm; the aqueous soluble [^{14}C]residues were not further analyzed (Table 12).

In the 213-day rotation, total [^{14}C]residues were 0.012 ppm in mature Swiss chard leaves, 0.013-0.014 ppm in turnip roots and leaves, 0.028 ppm in corn fodder, and were not detected in corn grain (Table 7). Total [^{14}C]residues were 0.007 ppm in immature corn silage and forage.

In the 361-day rotation, total [^{14}C]residues were 0.017 ppm in mature Swiss chard leaves, 0.008 ppm in turnip roots and leaves, 0.020 ppm in corn fodder, and were not detected in corn grain (Table 7). Total [^{14}C]residues were 0.008-0.009 ppm in immature corn silage and forage.

In the surface soil (9-12 inches) immediately posttreatment, [^{14}C]trifluralin was 0.738 lb ai/A in the field soil used for the 213-day rotation; 0.773 lb ai/A in the field soil used for the 30-day, 214-day, and 362-day rotations; and 0.818-0.863 lb ai/A in the greenhouse soil used for the 30-day rotation (Table 1). In the 30-day rotation greenhouse soil, [^{14}C]trifluralin was 0.56-0.60 lb/A at 30 days and 0.28-0.346 lb/A at approximately 110 days; in the field soil, [^{14}C]trifluralin was 0.284 lb/A at 30 days and 0.116 lb/A at approximately 180 days (Table 3). In the 108-, 174-, and 361-day rotation field soils, [^{14}C]trifluralin at planting and harvest (120-441 days posttreatment) ranged from 0.03 to 0.08 lb/A with no discernable pattern (Tables 5 and 7). In the 213-day rotation field soil (which was unique in being treated in the fall rather than spring), [^{14}C]trifluralin was 0.223 lb/A at 213 days and 0.18-0.20 lb/A at approximately 220-380 days (Table 7).

Air temperatures ranged from 21 to 103 F during the 30-day rotation; 40 to 103 F during the 108-day rotation; 22 to 103 F during the 174-day rotation; 2 to 95 F during the 213-day rotation; and 2 to 103 F during the 361-day rotation. Cumulative precipitation plus irrigation totaled 5.61 inches at 30 days, 19.54 inches at 108 days, 26.56 inches at 174 days, 39.43 inches at 213 days, and 63.46 inches at 361 days.

COMMENTS:

1. Storage stability data were not provided for trifluralin in the plant tissue, although samples were stored frozen for up to 1 year prior to analysis. The soil samples were not stored prior to extraction and analysis.

2. Based on comments made by the study author, it appears that although total [^{14}C]residues in the soil were measured, they were not reported. Rather, the study author reported only the concentration of [^{14}C]trifluralin in the soil, which was calculated from TLC and LSC data that were not submitted with the original document.

3. Immature samples of turnip and Swiss chard were not analyzed for trifluralin residues.

4. The soil sampling depth was reported as 9-12 inches. Concentrations in the soil were then determined on the basis of the weight of the sample rather than the volume.

5. The test site was plowed in June 1986 to turn under the sod covering. During the fall of 1986, several inches of sand were spread over the

area and incorporated into the soil to a depth of 9 inches. Winter wheat was planted as a cover crop in October 1986 and 1987, and was tilled into the soil in the spring of 1988 prior to the application of trifluralin.

6. The study author stated that the maximum registered application of trifluralin is 0.725 lb ai/A.

7. EFGWB prefers that [^{14}C]residues in samples be separated by chromatographic methods (such as TLC, HPLC, and GC) solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R_f of reference standards.

   In this study aliquots of the extracts were analyzed by one-dimensional TLC.

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